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Express Letter

Hard Magnetic Properties of (001) Oriented $L1_0$-FePd Nanoparticles Formed at 773 K

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Two-dimensionally dispersed 10 nm-sized Fe/Pd and Fe/Pt particles (nanoparticles) with orientations have been fabricated with the same condition using an electron-beam evaporation technique. Heat treatments at temperatures above 773 K lead to a formation of $L1_0$-type (CuAu I-type) FePd and FePt ordered alloy particles with sizes as small as 10 nm. In the case of FePt nanoparticles, coercivity started to increase at 873 K, while in the case of FePd at 773 K. Moreover, in most of the FePd nanoparticles, their c-axes oriented normal to the film plane and the perpendicular coercivity reached as high as 1.2 kOe after annealing at 773 K for 1 h. This method can be applied to fabricate ultra-high density magneto-optical or vertical recording media under low annealing temperatures for the $L1_0$-structure formation especially in the Fe-Pd system.

KEYWORDS: Iron-Palladium, Iron-Platinum, oriented nano-particles, transmission electron microscopy, atomic ordering, CuAu I-type superstructure, perpendicular anisotropy, hard magnetic properties

The magnetic recording density has been increasing every year, and it has reached nearly the maximum value for the conventional continuous magnetic film media.[1] As the candidates for the future ultra-high-density recording media, CoPt[2,3] and FePt[4–9] ordered alloy nanoparticles are now attracting much interest. These alloy nanoparticles have high uniaxial anisotropies related to their $L1_0$-type ordered structures (tetragonal CuAu I-type) with the axial ratios less than unity ($c/a \sim 0.96$). It is known that the ordered FePt has the uniaxial anisotropy constant (K_u) as high as 6.6×10^6 J/m^3 [10] or 1.6×10^7 J/m^3.[11] The high uniaxial anisotropy enables the hard magnetic nanoparticles by overcoming the thermal agitation of magnetic moments. However, according to recent reports,[3–7,9] not only FePt but also CoPt needs a high annealing temperature above 873 K for atomic ordering and the high temperature annealing condition is thought to be not suitable for industrial application. An equiatomic Fe–Pd alloy also has the $L1_0$-type ordered phase and has the K_u value as high as 1.8×10^6 J/m^3,[10] which is lower than that of FePt but larger than that of hcp-Co.[12] The present study aims at a fabrication of two-dimensionally dispersed $L1_0$-FePd nanoparticles with orientation and hard magnetic character under a low temperature annealing condition as low as 773 K.

The specimen fabrication process is the same as used in our previous study[4,6] for the formation of the oriented $L1_0$-FePt nanoparticles. The process took advantage of the overgrowth of Fe on Pd "seed" particles epitaxially grown on cleaved NaCl (001) substrates kept at 673 K. After the deposition, an amorphous (a-) Al_2O_3 film was further deposited to protect the particles from oxidation. In order to compare magnetic properties between the FePd and FePt particles, FePt nanoparticles on NaCl (001) were fabricated also under the same technique. According to the energy dispersive X-ray spectroscopy study, mean composition of FePd and FePt nanoparticles were 58 at%Pd and 52 at%Pt, respectively. Heat treatments of the as-deposited Fe/Pd and Fe/Pt specimens for the formation of atomically ordered nanoparticles (FePd and FePt) were made in a high-vacuum furnace ($<2 \times 10^{-5}$ Pa) at the same time in order to avoid a difference in annealing condition (673, 773 and 823 K for 1 h). The thermocouple attached to the furnace was calibrated with the melting temperature of pure aluminum. A part of each NaCl (001) substrate with the as-deposited and annealed films was immersed into distilled water and the removed film was mounted onto copper microgrid for later transmission electron microscope (TEM) observation operated at 200 and 300 kV. The magnetic hysteresis loops of both of the FePd and FePt nanoparticles on NaCl (001) substrates after the heat-treatment were measured using a superconducting quantum interference device (SQUID) magnetmeter.

Figure 1 shows the annealing temperature dependence of magnetic coercivity of FePd and FePt nanoparticles. An enhancement of magnetic coercivities of all specimens with elevated annealing temperatures is due to the proceeding of the atomic ordering reaction. In the case of FePd specimen, the perpendicular coercivity exceeded 1.2 kOe after annealing at 773 K for 1 h, though the in-plane coercivity was around 0.3 kOe. This indicates that most of the crystal c-axes of FePd

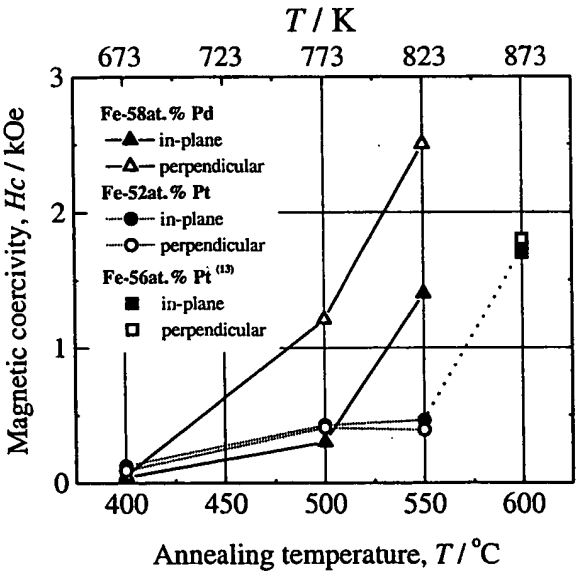

Fig. 1. Annealing temperature dependence of coercivity for both of FePd and FePt nanoparticles dispersed on NaCl (001) substrates covered by a-Al_2O_3 thin films. Coercivity of FePd nanoparticles abruptly increased at the temperatures above 773 K, while those of FePt above 873 K.

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particles are oriented normal to the film plane. The FePd specimen after annealing at 823 K for 1 h showed the perpendicular and in plane coercivities of 2.5 and 1.4 kOe, respectively. On the contrary, in the case of FePt specimen, both perpendicular and in-plane coercivities showed entirely lower values than those of the FePd specimen under the annealing temperature less than 823 K. To attain the high coercivity more than 1 kOe in the FePt specimen, the higher temperatures above 873 K were necessary.[13)]

A typical TEM image and the corresponding selected area electron diffraction (SAED) pattern for the film with Fe-58 at%Pd nanoparticles after annealing at 773 K for 1 h are shown in Figs. 2(a) and 2(b), respectively. The particle sizes are around 10 nm, and their particle dispersion is quite homogeneous. The FePd nanoparticles are isolated with each other by the covering a-Al_2O_3 film, and their inter-particle edge to edge distances are in the range of 5 to 10 nm. In Fig. 2(b), 110_{FePd} superlattice reflections are clearly seen, which means that the $L1_0$-type ordered phase of FePd was formed by annealing at 773 K. The axial ratio c/a was 0.97 according to the measurement using the related reflections in the SAED pattern. However, from a close examination of the diffraction pattern, very weak 001_{FePd} reflections could be observed in Fig. 2(b) (indicated by arrows). This means that the FePd particles with their crystallographic c-axes normal to the film plane are larger in number than those with the c-axes parallel to the film plane. In Fig. 2(c), a high-resolution transmission electron microscope image of an FePd nanoparticle indicated in Fig. 2(a) is shown. The lattice image of the nanoparticle with the crystallographic c-axis normal to the film is seen. It is noted that the ordered-lattice fringes with the spacing of 0.27 nm are not widely spread in the particle, meaning that the atomic ordering reaction was not completed in the particles. In Fig. 2(d), a Fourier transform of the image in Fig. 2(c) is shown. From the TEM observations, single crystal nanoparticles with c-axis normal to the film plane could be observed frequently, while those with c-axis parallel to the film plane could be observed once in a while. This structural feature coincides with the higher value of perpendicular coercivity of the film compared with the in-plane one. On the contrary, in the case of FePt nanoparticles, both 110_{FePt} and 001_{FePt} reflections appeared with almost the same intensity after annealing at 773 K for 1 h. According to our close observation of the nanoparticles, any one of the three ⟨100⟩ axes of the parent fcc-FePt acted as the tetragonal c-axis of the $L1_0$ structure and three-variants domain structures were formed in each nanoparticles. These domain structures clearly appeared at the initial stage of annealing at 873 K and disappeared after 24 h to form single or two-variant domains.[13)] The reason why the variants of domain structures are formed in FePt nano-particles and are not formed in the FePd case is not clear at this time. The detailed analysis of nanostructures and their relations to the magnetic properties in the oriented FePd and FePt nanoparticles are now in progress.

In the present study, the possibility for fabricating the oriented $L1_0$-FePd nanoparticles under the lower annealing temperatures for the atomic ordering has been examined. Fe-58 at%Pd nanoparticles showed a low annealing temperature as low as 773 K and showed a perpendicular coercivity of 1.2 kOe. This annealing temperature is about 100 K lower than that for the nanoparticle FePt specimen. From the TEM observation, it was found that the single-variant 10 nm-sized FePd particles with c-axes normal to the film plane were predominant in number different from our previous FePt case.

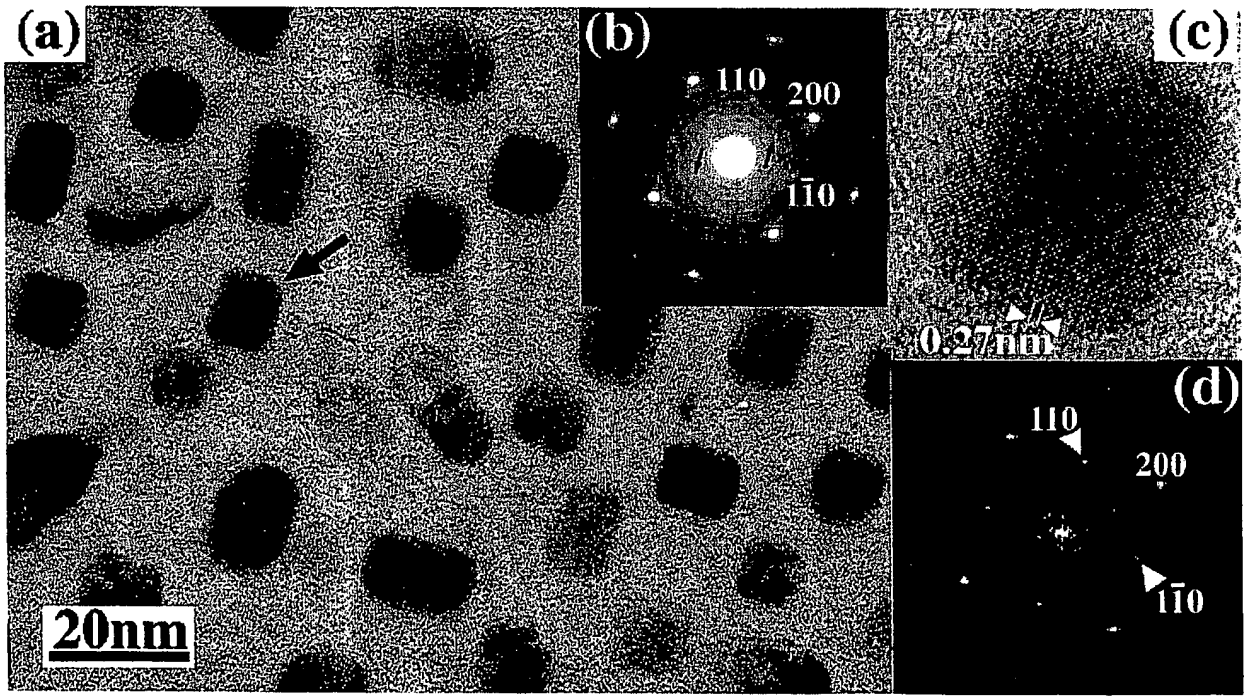

Fig. 2. (a) TEM micrograph and (b) the corresponding SAED pattern for FePd nanoparticles dispersed on a-Al_2O_3 film. 110_{FePd} superlattice reflection can be clearly seen, while 001_{FePd} is almost invisible. (c) Magnified lattice image of an FePd nanoparticle marked by an arrow in (a) and (d) its Fourier transformed pattern.

This is the origin of the high perpendicular anisotropy of the present FePd films.

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